In-situ Three-dimensional Visualization of Precipitation Behavior in a Porous Air Electrode for Aqueous Lithium-air Battery

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ABSTRACT

The aqueous lithium-air battery is receiving considerable research attention because of its high theoretical energy density; however, discharge products tend to precipitate and inhibit the chemical reaction in the battery. To clarify the precipitation mechanism, the precipitated discharge products in a carbon-based porous air electrode were visualized three-dimensionally by oblique soft X-ray computed tomography. As a result, precipitation of the discharge products was observed clearly. The precipitate did not dissolve entirely and bubbles emerged in the air electrode during the charging process. This indicates that the charge/discharge products degrade the cycling performance of the aqueous lithium-air battery.

Keywords : Lithium-air Battery, Precipitation, Soft X-ray, Porous Electrode

1. Introduction

Lithium-air batteries receive significant research interest because the theoretical energy density of a lithium metal electrode is the highest of all solid electrodes.1 This property is important from the perspective of enabling electric vehicles to rival the performance of gasoline-powered vehicles.

In this study, we focus on the aqueous lithium–air secondary battery. One serious problem with this type of battery is the precipitation of the discharge products. The precipitate covers the surface of the porous air electrode (which is composed of carbon fiber) during long discharge processes. Transport phenomena in the air electrode on discharge are then blocked by the precipitate and this causes cell performance degradation.2 The precipitation behavior in an aqueous lithium air battery is an important factor in maintaining stable cell performance during long discharge processes.

In this study, the distributions of the precipitation of the discharge products inside the air electrode were observed using an oblique soft X-ray computed tomography (CT) system.

2. Experimental

2.1 Oblique soft X-ray computed tomography

X-ray radiography enables nondestructive observation of the porous air electrode. In the conventional X-ray range (>100 keV), the discharge product (LiOH·H2O or Li2O3) in the aqueous electrolyte cannot be detected; however, use of the soft X-ray range (1–10 keV) effectively improves the detection of the discharge product because of the sensitivity of the attenuation coefficient for this X-ray range.3,4

To visualize the distribution of the precipitation in three dimensions, an oblique cone-beam CT method was used.5 This system is suitable for visualization of a conventional cell, which is thin and broad. As a combined visualization system, the TUX-3110 (Mars Tohken Solution Co., Tokyo, Japan) was used in this study.5,6

2.2 Cell structure and conditions

Figure 1 shows the structure of the experimental cell used to visualize the precipitation of the discharge products. The Li-metal anode was water-stable and had a multilayer structure for the aqueous lithium air battery.6 LATP [Li1+x/2Al1-T/2Si3/2P3/2ₓ₋₁] (Ohara Co., Kanagawa, Japan), which is a water-stable lithium-ion-conducting glass ceramic, was used, along with PEO18LiTFSI [poly(ethylene oxide) with lithium bis(trifluoromethanesulfonyl) imide] as the organic electrolyte.7 The thicknesses of the lithium metal, PEO, and LATP layers were 150, 300, and 150 µm, respectively.

For the air electrode, SIGRACET® 10AA (SGL Group, USA) was used as the carbon porous layer with no catalyst. The average fiber diameter was approximately 20 µm. To induce precipitation more rapidly, saturated LiOH (aq) was used as the aqueous electrolyte.

Soft X-ray irradiation was performed in the vertical direction, and a hole was formed in the bottom of a poly(tetrafluoroethylene) petri dish to increase the intensity of the soft X-rays. The hole was covered with polyimide tape. The reaction area was 5 mm × 5 mm.

All experiments were performed at 60°C,8 and the cell was kept under high-humidity conditions to prevent evaporation of the aqueous electrolyte. The current density was 0.5 mA/cm². The charge/discharge cycle was stopped during CT imaging (the measurement time was 48 min).

3. Results and Discussion

3.1 Precipitation behavior (discharge process)

First, the precipitation behavior during the discharge process was visualized, and the results are shown in Fig. 2. The reconstructed three-dimensional images are shown as the same cross-sectional images in the air electrode in each case.

Figure 2(a) shows the initial condition of the air electrode when saturated with the aqueous electrolyte. Because the aqueous electrolyte absorbed much more of the soft X-rays than the carbon fibers, the remarkable structure of the carbon fibers was not observed. However, after the discharge, several carbon fibers could
be clearly observed [as shown in Fig. 2(b)]. It is thought that the precipitation occurred on the carbon fibers and that the precipitated discharge products (LiOH·H$_2$O(s) or Li$_2$O$_2$) absorbed more of the soft X-rays than the electrolyte (LiOH (aq)). The precipitation distribution did not change, even as the discharge process progressed.

3.2 Reaction product behavior (discharge/charge cycle)

The reaction product behavior during the discharge and charge cycles was also observed. The discharge and charge cycle tests were performed three times, and the cycle times were 1 h for discharging and 1 h for charging.

After the discharge/charge cycle, fibers with strong contrast and bubbles were observed in the same cross-sectional image [as shown in Fig. 3(a) and (b)]. Theoretically, the solubility around the precipitate should be maintained, so the precipitate should dissolve in the aqueous electrolyte after the charging process, because the ion concentration around the precipitate becomes lower than the precipitate’s solubility. However, the experimental results show that the precipitate did not dissolve immediately, even after the charging process. It is believed that the precipitate dissolution rate was slower than the ion diffusion rate. The ions that were needed for the charge reaction were supplied from the bulk of the aqueous electrolyte, where the ion concentration was higher.

The bubbles were observed over a wide area above the precipitation layer [as shown in Fig. 3(c) and (d)]. These bubbles were only generated after the charging process, and thus were considered to be oxygen bubbles. Oxygen has low solubility and a large molar volume; therefore, oxygen was expected to be produced as bubbles, occupying large amounts of space and displacing the electrolyte. As a result, the bubbles inhibited the chemical reaction by causing the carbon fiber surfaces to dry out.

Figure 4 shows the charge/discharge curve of the experimental cell. The overpotential in the charge/discharge process increased after every cycle. It was thought that the overpotential was caused by the combination of the reaction products: precipitated LiOH·H$_2$O(s)/Li$_2$O$_2$ and bubbles.

4. Conclusion

In this study, the precipitation of discharge products and bubbles in an air electrode that was saturated with an aqueous electrolyte for...
an aqueous lithium air battery were visualized by oblique soft X-ray CT. The visualization process showed that during precipitation after the discharge process, the discharge products only precipitated on specific fibers in the air electrode.

Visualization of the reaction products after a discharge/charge cycle showed that the precipitate did not disappear and that the bubbles appeared in the air electrode. It is believed that the precipitate did not dissolve immediately because of its low dissolution rate, and that the oxygen bubbles were produced by the charge reaction. The charge/discharge curve also indicated that the cell performance was affected by the reaction products.

Detailed investigations of the effects of the structure of the air electrode on precipitation and bubble formation during long discharge processes must therefore be performed.

References


Figure 4. (Color online) Charge-discharge performance of the experimental cell. Theoretical voltage is 3.45 V at pH = 14.0.